this group of chemicals have shown excellent properties in improving the wetting action of enzyme desizing baths without retarding the activity of the enzymes. Such products are of considerable interest for use in the desizing of cotton piece goods.

Because of the presence of the ester linkage in the molecule, these products are not generally applicable with good results for usage either in strongly alkaline solutions, such as used in the mercerization and kier boiling of cotton, or in strongly acid solutions, such as used for carbonizing of wool and the pickling of steel. They are recommended for use in the pH range of 5 to 11 and show optimum performance between pH 7 and pH 9.

In the treatment of paper towels it has been found that the use of selected chemicals from this group give a marked increase in the rate of moisture absorbency of the toweling. However, these encouraging results are not realized to a sufficient degree when urea formaldehyde and melamine formaldehyde resins are incorporated in the pulp to give high wet strength to the toweling. Under such conditions the alkyl aroyl sulfoproprionates are less effective than surface active agents having greater stability in acid solutions. Application of these products in fields other than textile and paper is now being developed. They have a potential wide range of usage, varying from dishwashing compounds to agents for wetting down coal, and will undoubtedly find outlets in many industries.

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Electrolytic Production of *gem*-Dinitroparaffins

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IN THE course of a series of studies on the reactions of the nitroparaffins and their derivatives, the products formed by electrolysis of solutions of nitroparaffins in aqueous alkali have been investigated. Primary nitroparaffins were found to yield α-dinitroparaffins and nitro olefins under the proper conditions (*1*). 2-Nitropropane has been reported to give a small yield of α-dinitroparaffin (*4, 5*). In Zelinsky's experiments (*6*) this product was accompanied by an oil to which he assigned the formula $C_6H_{12}N_4O_8$. Further study of the electrolysis of concentrated solutions of secondary nitroparaffins in aqueous alkali in a divided cell, using a polished platinum anode, has shown that *gem*-dinitroparaffins can be obtained in significant quantities. An attempt to increase the yield of *gem*-dinitro compound by the addition of a nitrite salt to the anolyte before electrolysis was successful in increasing the ratio of *gem*-dinitroparaffin to α-dinitroparaffin among the products to approximately 3 to 1. Without attempting to establish a detailed mechanism for the reaction, the over-all effect may be represented by the simple equation

$$RR'CNO_2^- + NO_2^- \longrightarrow 2e + RR'C(NO_2)_2 \tag{1}$$

McCracken (*2*) has disclosed that dinitroparaffins having both nitro groups attached to the same carbon atom improve the cetane number of Diesel fuels. McCracken (*2*) and Nygaard (*3*) have claimed 2,2-dinitropropane to be outstandingly superior to other *gem*-dinitroparaffins. According to the data in tables in the cited patents, the longer chain dinitro compounds are inferior to those having short chains, not only in that the molecular weight is higher but that the improvement in cetane number per 0.01 mole per kilogram of fuel is inferior when equal percentage compositions of 1,1-dinitroethane and 1,1-dinitroheptane are compared. On the other hand, the data in Table I, based on tests carried out in the Socony-Vacuum Laboratories, show 1,1-dinitrocyclohexane to be slightly superior to 2,2-dinitropropane when compared on the latter basis. However, pound for pound the dinitropropane was more effective.

TABLE I. DIESEL FUEL TESTS

Compound Blended with Base Fuel	Wt. %	Cetane Number	ΔCN[a]	ΔCN/0.01 Mole/ Kg.	ΔCN/ Gram/ Kg.
None (blank)		41.2			
1,1-Dinitro-cyclohexane	0.10	43.6	2.4	4.2	2.4
	0.25	45.1	3.9	2.7	1.6
	0.50	46.8	5.6	2.0	1.1
	0.72	48.1	6.9	1.7	0.96
2,2-Dinitro-butane	0.10	43.3	2.1	3.1	2.1
	0.25	44.7	3.5	2.1	1.4
	0.50	47.1	5.9	1.8	1.2
2,2-Dinitro-propane	0.25	45.9	4.7	2.5	1.9
	0.50	48.1	6.9	1.9	1.4

[a] Change in cetane number.

EXPERIMENTAL

The cathode employed was a copper wire spiral immersed in 25% aqueous sodium hydroxide in a 27-mm. diameter alundum cup. The anode was polished platinum foil. The cathode cup and anode were placed against the opposite sides of the beaker containing the anolyte. The size of the beaker was just sufficient to contain the anolyte when filled to a depth of about 6 cm. The temperature was controlled by means of a water bath.

The products reported below were previously known compounds and were identified by their physical and chemical properties. The yields listed are yields of crude products before final purification.

ELECTROLYSIS OF 2-NITROBUTANE SOLUTION. A solution prepared by mixing at 70° to 90° C. 126 grams of 2-nitrobutane with a solution of 55 grams of sodium hydroxide in 100 grams of water was electrolyzed at 23° to 37° C. at 6 to 10.5 volts and 1.5 to 4.0 amperes for a sufficient time to be equivalent to 16 hours at 8 volts and 4 amperes. It yielded 85 grams of oil, d_4^{25} 1.08. Vacuum distillation of the product indicated that it consisted of about 70% 3,4-dinitro-3,4-dimethylhexane, which had a melting point of 78.5° to 79.0° C., and about 20% 2,2-dinitrobutane, which had a boiling point of 194° to 198° C. at 740 mm., with a small amount of lower boiling materials.

A solution prepared by stirring 40 grams of 2-nitrobutane at 70° C. with 25 grams of sodium hydroxide in 56 grams of water was mixed with 42.5 grams of sodium nitrite in 40 ml. of water. The resulting anolyte was electrolyzed 8.5 hours at 9 to 11 volts and an average of 3.8 amperes at 37° to 47° C. using a 20-sq. cm. platinum foil anode. The 26.6 grams of oil produced, d_4^{25} 1.18, was shown by vacuum distillation to contain 70 to 80% 2,2-dinitrobutane and 15 to 20% 3,4-dinitro-3,4-dimethylhexane.

ELECTROLYSIS OF 2-NITROPROPANE SOLUTIONS. In a large number of electrolyses of solutions of 2-nitropropane in aqueous alkali under various conditions, the 2,3-dinitro-2,3-dimethylbutane produced was accompanied by varying amounts of 2,2-dinitropropane when the anode was a polished platinum foil, but very little if any 2,2-dinitropropane was obtained when the anode was graphite. As in the case of 2-nitrobutane, the addition of an excess of sodium nitrite to the anolyte resulted in increasing the yield of *gem*-dinitro compound at the expense of the α-dinitro compound, so that the latter accounted for less than 25% of the total weight of product, which was 50% of the weight of the 2-nitropropane.

ELECTROLYSIS OF NITROCYCLOHEXANE SOLUTIONS. Using an excess of sodium nitrite, 64.2 grams of nitrocyclohexane yielded 3 grams of cyclohexanone, 5 grams of 1,1′-dinitrodicyclohexyl, and 15 grams of 1,1-dinitrocyclohexane.

DISCUSSION

It seems probable that the liquid to which Zelinsky assigned the formula $C_6H_{12}N_4O_8$ was really $C_3H_6N_2O_4$, 2,2-dinitropropane, which would have the same percentage composition. The fact that added sodium nitrite increases the yield of *gem*-dinitro compound suggests that nitrite ions, formed either during the preparation of the solution or during the electrolysis, may account for the *gem*-dinitro compounds obtained when no nitrite has been added purposely.

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Preparation of Terpeneless Essential Oils

A CHROMATOGRAPHIC PROCESS

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ESSENTIAL oils are widely used in perfumes, pharmaceuticals, toilet preparations, and as flavors in food products and beverages. These natural oils contain terpenes and sesquiterpenes, which in general oxidize readily in the air with the development of unpleasant odors and flavors. In order to alleviate this difficulty, the producers of essential oils have placed on the market the so-called terpeneless and sesquiterpeneless oils. These, for the most part, contain oxygenated compounds, which are more stable and contain most of the odor and flavor of the original oil.

Commercially the terpeneless oils are produced by fractional distillation, by extraction of the oxygenated compounds with dilute alcohol or other solvents, or by a combination of these two methods (*6*). These methods, however, have several disadvantages; most notable among these is that the application of heat, in fractional distillation, has a deleterious effect on the flavor and odor of the oil. Further, because of the complex mixtures and the similarity of boiling points of the components of the oils, the terpenes cannot easily be removed quantitatively from the oils, and conversely some of the oxygenated components are removed with the terpenes. This inadequacy of separation is also typical of the extraction method.

In working with the flavoring constituents in citrus fruits, it was noticed, on chromatographing numerous compounds on silicic acid chromatostrips (*9*), that such solvents as hexane left oxygenated compounds tightly adsorbed at the bottom of the chromatogram while moving hydrocarbons quite readily. The chromatostrip method consists in forming a thin layer of adsorbent on a glass strip, adsorbing a small sample of the material to be resolved near the bottom, and developing the column by immersing the bottom end in a test tube containing a small amount of solvent. Because the chromatostrips duplicate the performance of larger chromatographic columns, it was thought that adsorption could be applied to the commercial preparation of terpeneless citrus oils or more generally to the separation of hydrocarbons from the oxygenated constituents of any essential oil.

PRODUCTION OF TERPENELESS OILS

Two methods were used in applying adsorption principles to the production of terpeneless oils. In the first method a column of adsorbent was prepared by packing the conventional Tswett chromatographic tube with silicic acid (100 mesh or finer). Best results were obtained by packing the column from a slurry of the solvent with the adsorbent. The oil from which the terpenes were to be removed was then placed on the top of the adsorbent and drawn into it by suction. The column was developed in the usual